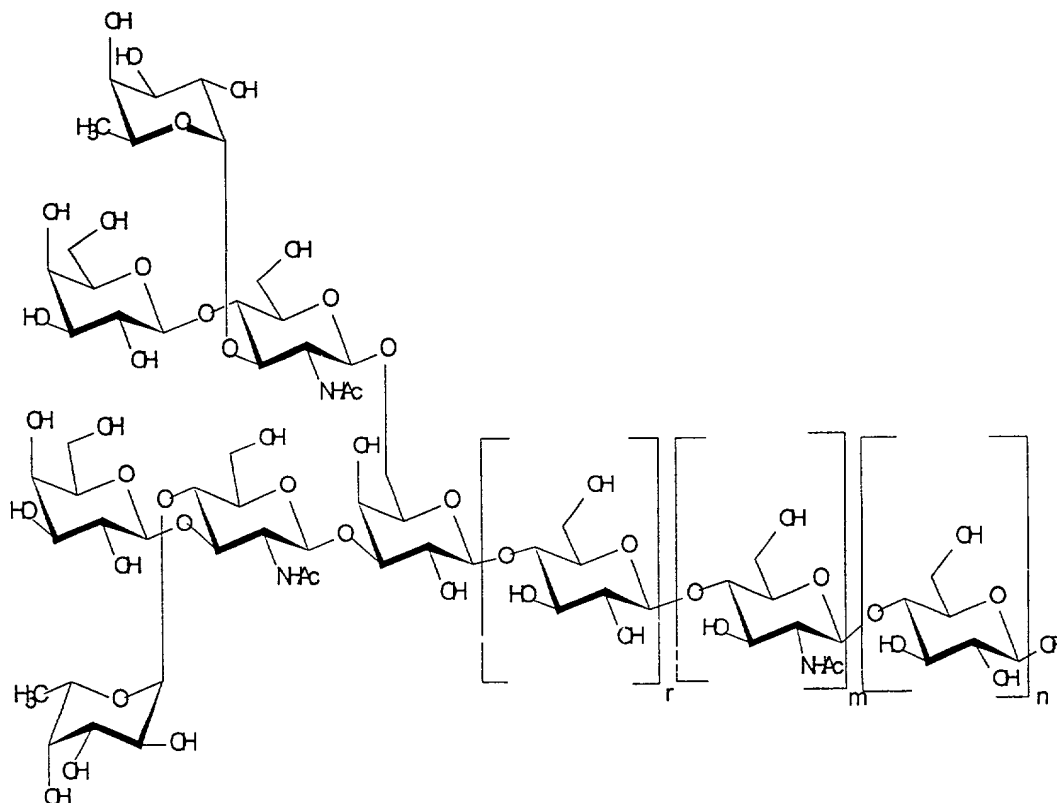


5 What is claimed is:

6 1. A compound having the structure:

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12 wherein R is H, substituted or unsubstituted alkyl, aryl or allyl, or an
13 amino acyl moiety, an amino acyl residue of a peptide, an amino acyl
14 residue of a protein, which amino acyl moiety or residue bears an ω -
15 amino group or an ω -(C=O)- group, which group is linked to O via a
16 polymethylene chain having the structure $-(CH_2)_s-$, where s is an
17 integer between about 1 and about 9, or a moiety having the
18 structure:

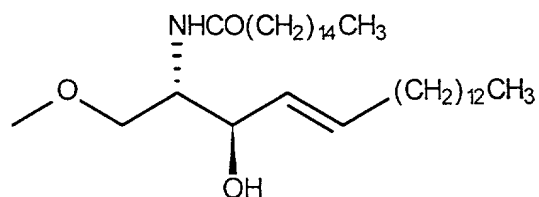
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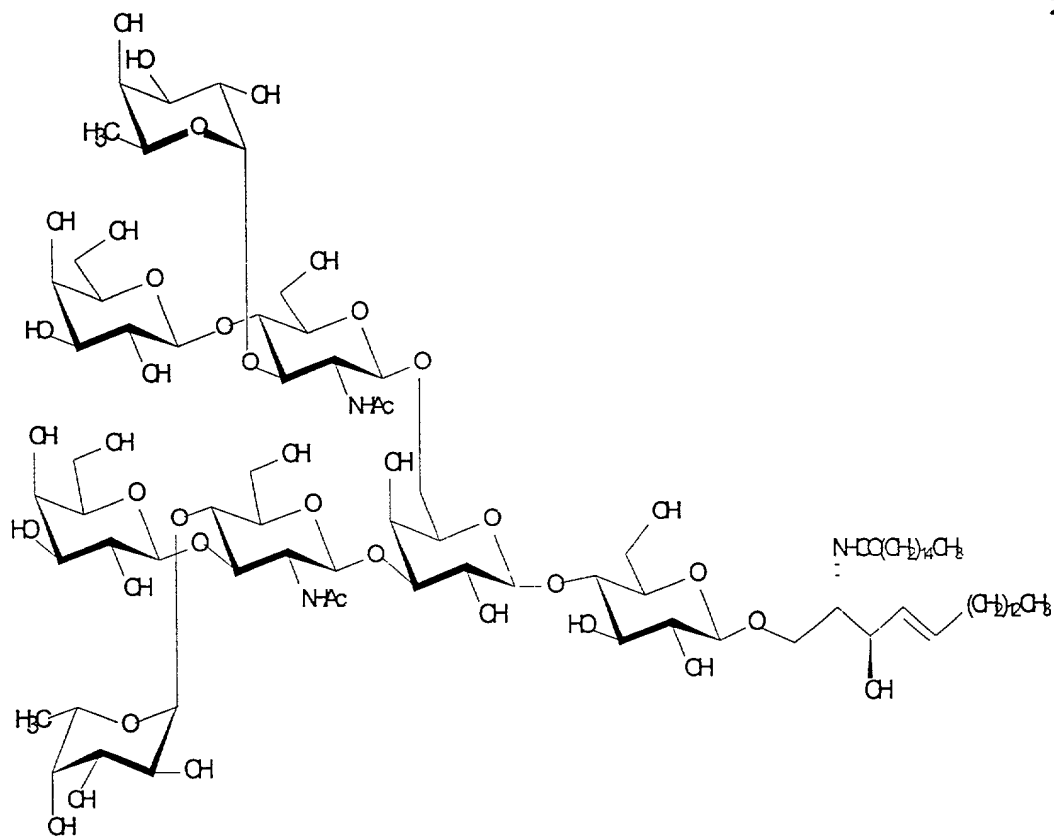


23 and wherein r , m and n are independently 0, 1, 2 or 3.

1 2. The compound of claim 1 having the structure:

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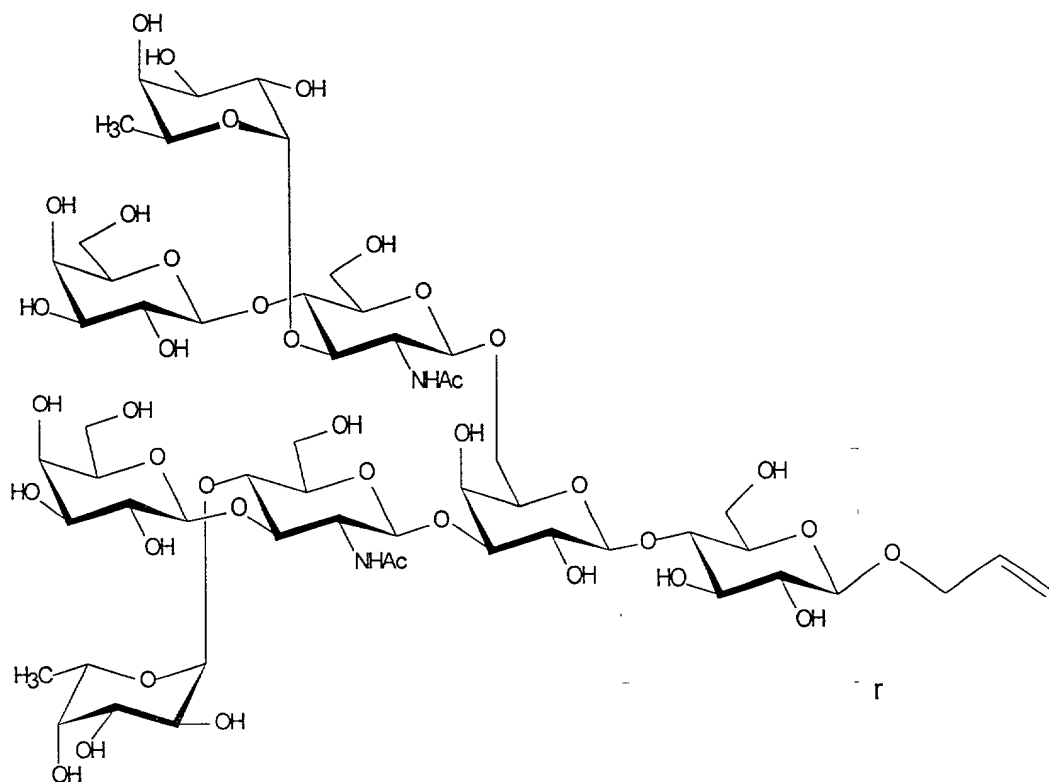
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1 3. The compound of claim 1 wherein the protein is bovine serum albumin
2 or KLH.

1 4. A compound having the structure:

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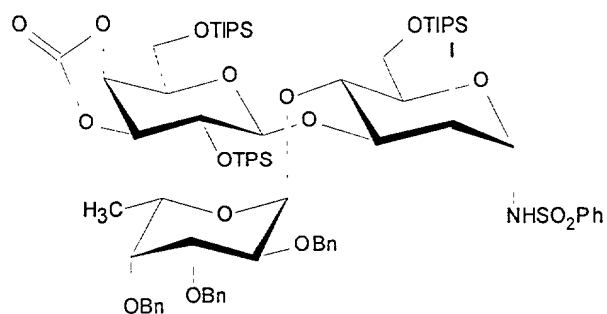
1
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2
3



5. The compound of claim 4 wherein r is 1.

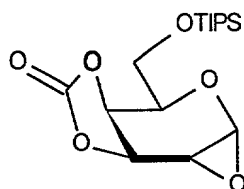
5. The compound of claim 4 wherein r is 1.

6. A method of preparing a trisaccharide iodosulfonamide having the structure:



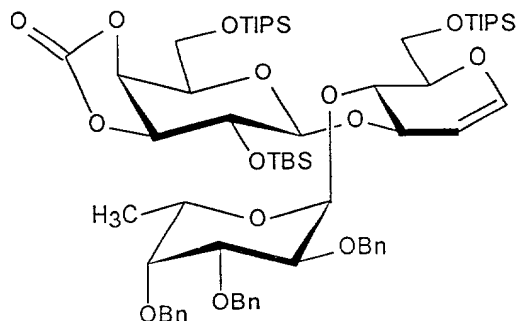
which comprises:

- (a) (i) coupling a disaccharide glycal with an epoxide having the structure:



under suitable conditions to form a trisaccharide intermediate; and

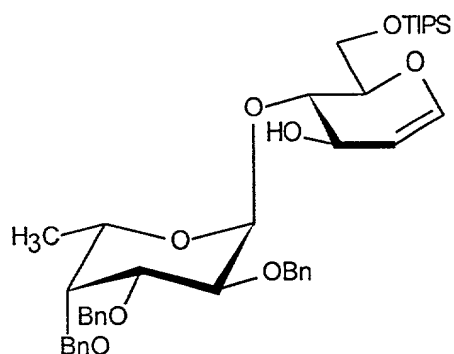
- (ii) etherifying the trisaccharide intermediate with a suitable protecting agent to form a trisaccharide glycal having the structure:



and

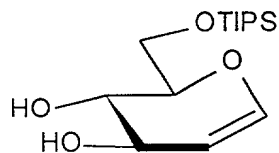
- (b) reacting the trisaccharide glycal formed in step (c) with an iodosulfonamidating agent under suitable conditions to form the trisaccharide iodosulfonamide.

7. The method of claim 6 wherein the disaccharide glycal having the structure:

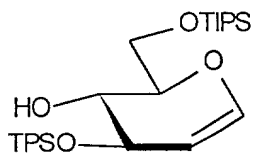


is prepared by a process which comprises:

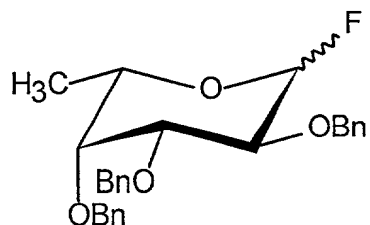
- (a) protecting a glucal having the structure:



with a silylating agent under suitable conditions to form a protected glucal having the structure:



- (b) (i) alkylating the protected glucal formed in step (a) with a fucosylfluoride having the structure:



and

- (ii) deprotecting under suitable conditions to form the disaccharide glycal.

8. The method of claim 7 wherein the silylating agent in step (a) is triphenylsilyl chloride.

9. The method of claim 7 wherein the alkylating step is effected in the presence of an ionizing salt, and the ionizing salt is AgClO_4 .

10. The method of claim 7 wherein the conditions of the deprotecting step comprise a base.

11. The method of claim 10 wherein the base is potassium carbonate.

12. The method of claim 6 wherein the conditions of the coupling comprise an acid.

13. The method of claim 6 wherein the acid is a Lewis acid.

1 14. The method of claim 13 wherein the Lewis acid is zinc dichloride.

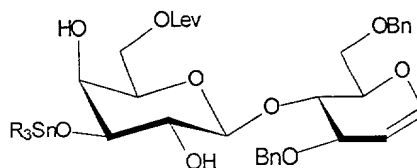
1 15. The method of claim 7 wherein the protecting agent is TBSOTf.

1 16. The method of claim 6 wherein the iodosulfonamidating agent of step
2 (b) comprises $I(coll)_2ClO_4$ and $PhSO_2NH_2$.

1 17. A method of preparing a disaccharide stannane having the structure:

2

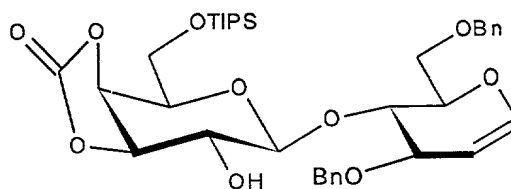
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4 which comprises:

5 (a) (i) deprotecting a disaccharide glucal having the structure:

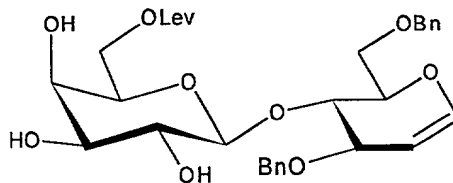
6



7 under suitable conditions to form a deprotected
8 intermediate; and

9 (ii) selectively reprotecting the deprotected intermediate with
10 levulinic acid under suitable conditions to form a
11 disaccharide levulinate having the structure:

12



13

and

14

(b) reacting the disaccharide levulinate formed in step

15

(a) with a distannyl oxide having the formula

16

 $(R_3Sn)_2O$, wherein R is linear or branched chain

17

alkyl or aryl, under suitable conditions to form the

18

disaccharide stannane.

1

18. The method of claim 17 wherein the conditions of the deprotecting step comprise a fluoride salt.

2

1

19. The method of claim 18 wherein the fluoride salt is a tetraalkylammonium fluoride.

2

1

20. The method of claim 19 wherein the tetraalkylammonium fluoride salt is tetra-n-butylammonium fluoride.

2

1

21. The method of claim 17 wherein the conditions of the reprotecting step comprise 2-chloro-1-methylpyridinium iodide.

2

1

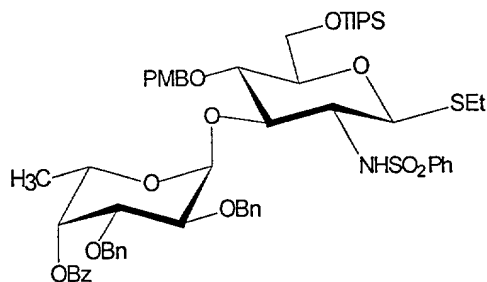
22. The method of claim 17 wherein R is n-Bu.

1

23. A method of preparing a disaccharide ethylthioglycoside having the structure:

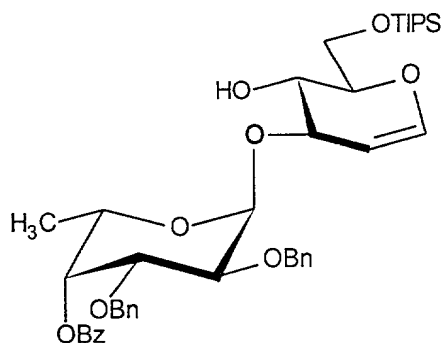
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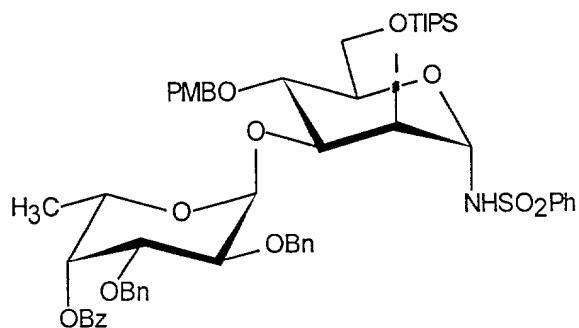
which comprises:

(a) (i) protecting a disaccharide glucal having the structure:



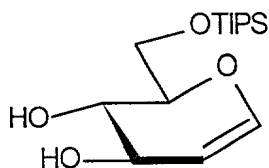
with a suitable protecting agent to form a protected disaccharide glucal; and

(ii) reacting the protected disaccharide glucal under suitable conditions with an iodosulfonamidating agent to form a disaccharide iodosulfonamide having the structure:

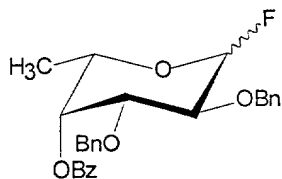


- 25 and
- 26 (b) treating the disaccharide iodosulfonamide formed in step (a)(ii)
- 27 with ethanethiol under suitable conditions to form the
- 28 disaccharide ethylthioglycoside.

- 1 24. The method of claim 23 wherein the disaccharide glucal is prepared by
- 2 a process which comprises:
- 3 (a) alkylating a protected glucal having the structure:



- 10 with a fucosyl fluoride having the structure:

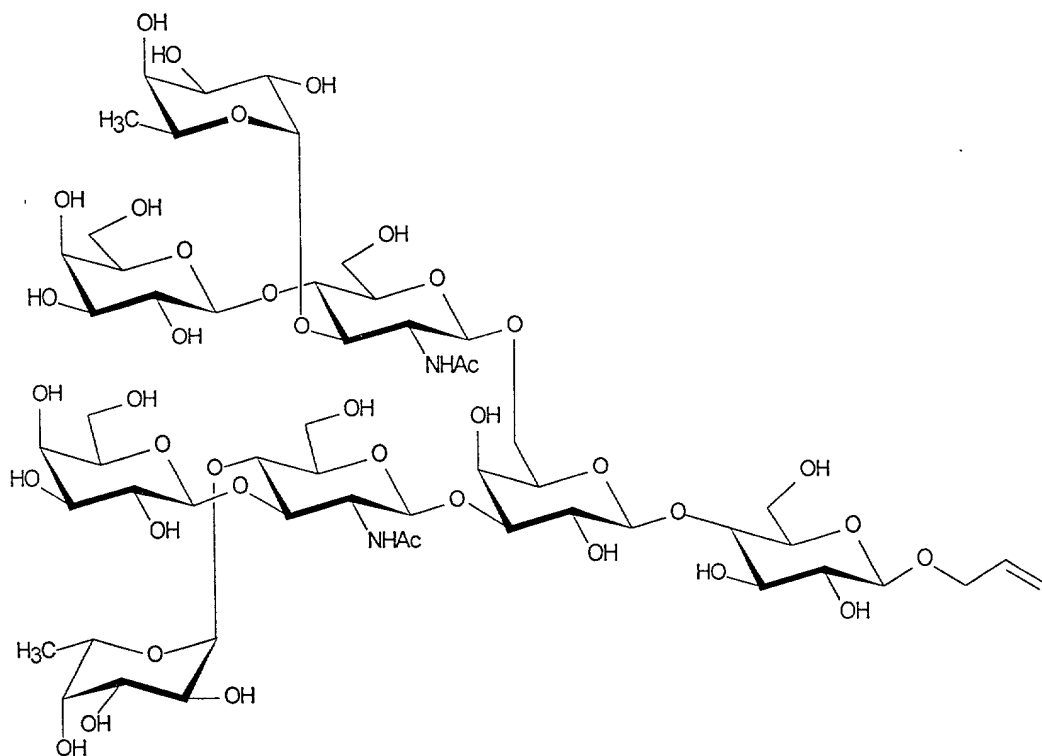


- 13 under suitable conditions to form the disaccharide glucal.

- 1 25. The method of claim 24 wherein the conditions of the alkylating step
- 2 comprise an ionizing salt.

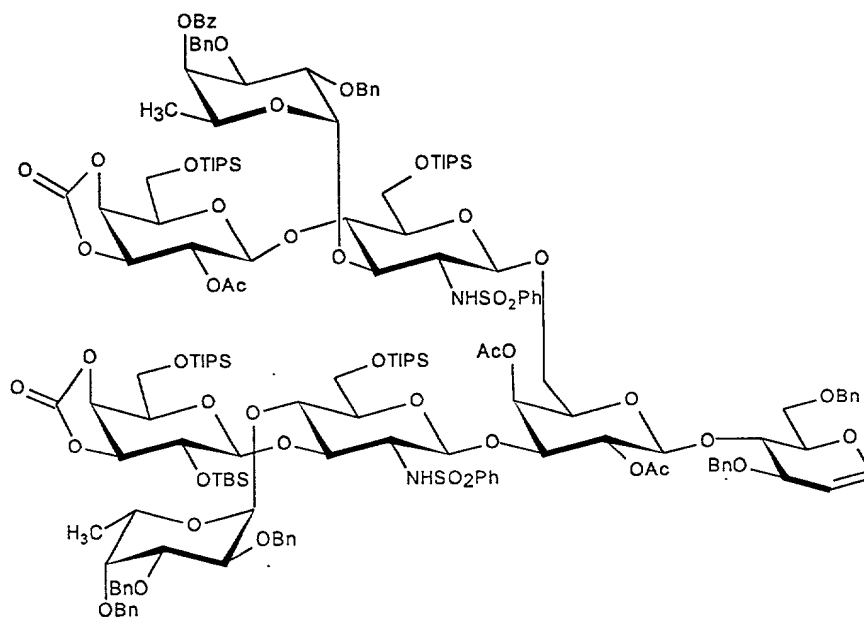
- 1 26. The method of claim 25 wherein the ionizing salt is AgClO_4 .

- 1 27. The method of claim 23 wherein the protecting agent is PMBCl.
- 1 28. The method of claim 23 wherein the iodosulfonamidating agent in step
2 (b)(ii) comprises $I(coll)_2ClO_4$ and $PhSO_2NH_2$.
- 1 29. The method of claim 23 wherein the conditions of the treating step
2 comprise a base.
- 1 30. The method of claim 29 wherein the base is LHMDs.
- 1 31. A method of preparing an N3 allyl glycoside having the structure:



which comprises:

(a) desilylating a protected N3 glycal having the structure:

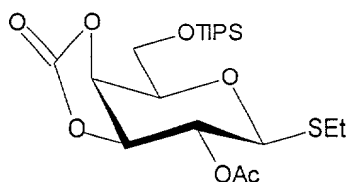


under suitable conditions to form a desilylated N3 glycal;

(b) deprotecting the desilylated N3 glycal formed in step (a) under suitable conditions to form a deprotected N3 glycal;

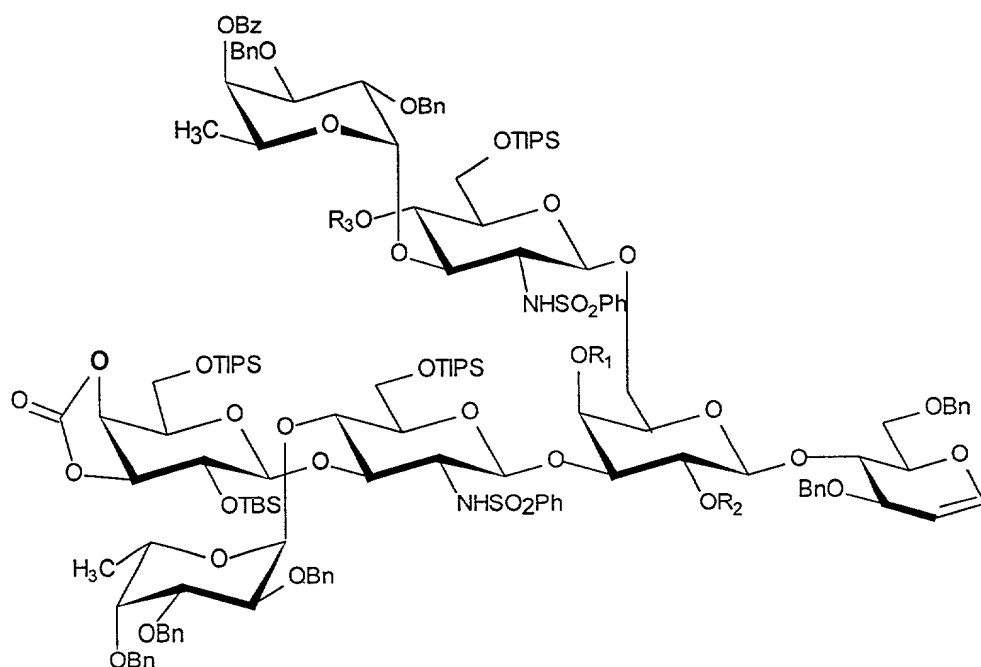
- 14 (c) treating the deprotected N3 glycal formed in step (b) with acetic
 15 anhydride in the presence of a suitable catalyst to form an N3
 16 glycal acetate;
 17
 18 (d) epoxidizing the N3 glycal acetate formed in step (c) with an
 19 oxygen transfer agent under suitable conditions to form an N3
 20 glycal epoxyacetate;
 21
 22 (e) cleaving the N3 glycal epoxyacetate formed in step (d) with allyl
 23 alcohol under suitable conditions to form an N3 glycal allyl
 24 ether; and
 25
 26 (f) saponifying the N3 glycal allyl ether under suitable conditions to
 27 form the N3 allyl glycoside.

- 1 32. The method of claim 31 wherein the protected N3 glycal is prepared
 2 by a process which comprises coupling an ethylthioglycoside having
 3 the structure:



- 5 with a heptasaccharide glycal having the structure:

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wherein R_1 and R_2 are Ac and R_3 is H, in the presence of an alkylating agent under suitable conditions to form the protected N3 glycal.

1 33. The method of claim 32 wherein the alkylating agent is MeOTf.

1 34. The method of claim 32 wherein the conditions of the desilylating step
2 comprise a fluoride salt.

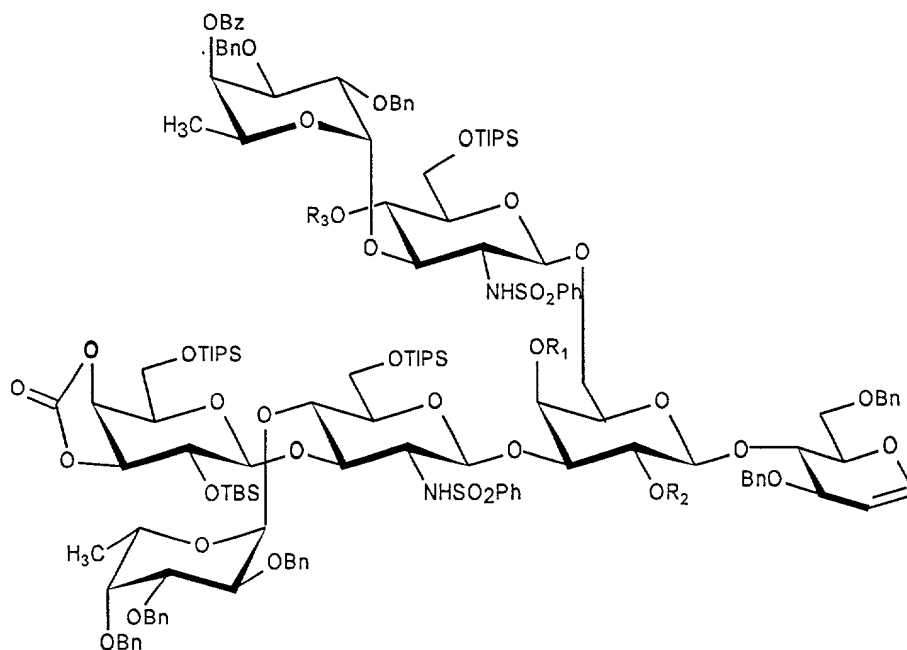
1 35. The method of claim 34 wherein the fluoride salt is a
2 tetraalkylammonium fluoride.

1 36. The method of claim 35 wherein the tetraalkylammonium fluoride is
2 tetra-n-butylammonium fluoride.

1 37. The method of claim 31 wherein the catalyst in the treating step is 2-
2 N,N-dimethylaminopyridine.

38. The method of claim 31 wherein the oxygen transfer agent is 3,3-dimethyldioxirane.

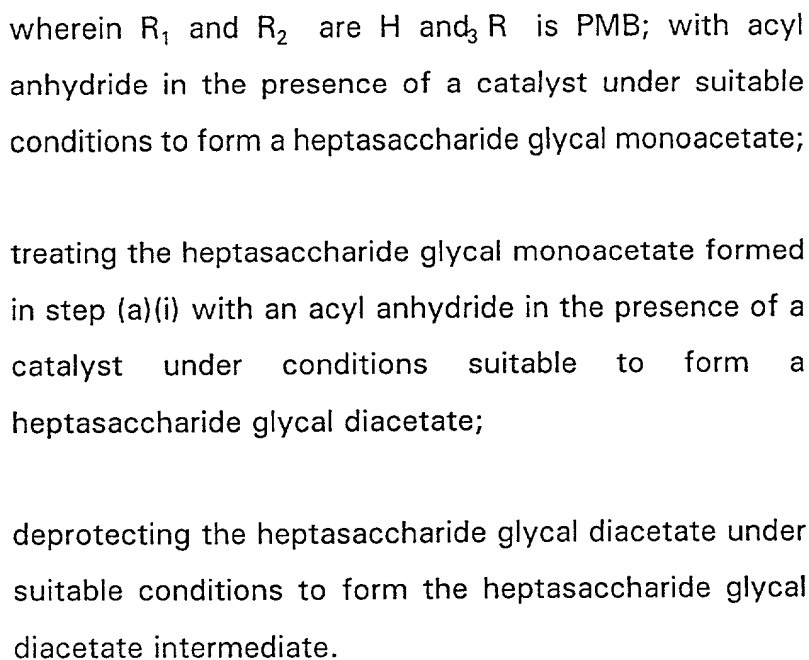
39. A method of preparing a heptasaccharide glycal diacetate intermediate having the structure:



wherein R_1 and R_2 are Ac and R_3 is H,
which comprises:

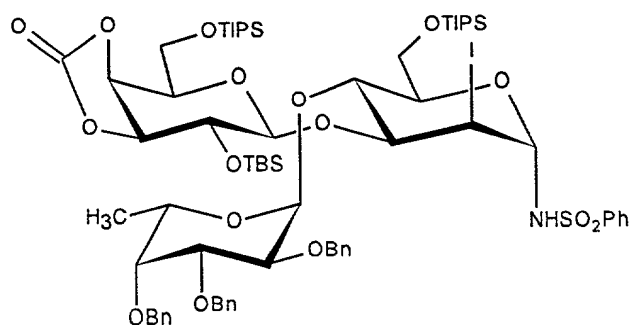
(a) (i) monoacylating a heptasaccharide glycal having the structure:

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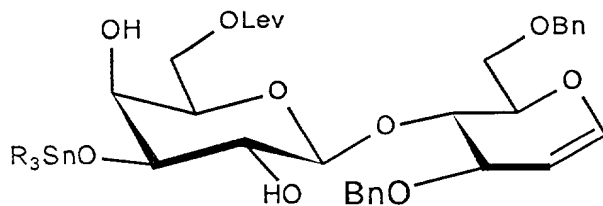


40. The method of claim 39 wherein the heptasaccharide glycal is prepared by a process which comprises:

(a) (i) reacting a trisaccharide iodosulfonamide having the structure:



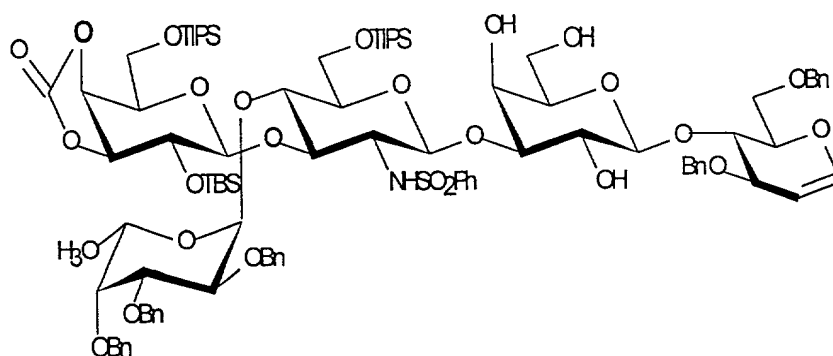
with a disaccharide stannane having the structure:



under suitable conditions; and

(ii) deprotecting under suitable conditions to form a pentasaccharide glycal having the structure:

12



13

and

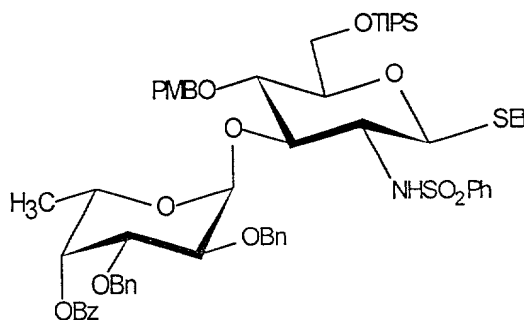
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(b)

coupling the pentasaccharide glycal formed in step (a)
with an ethylthioglycoside having the structure:

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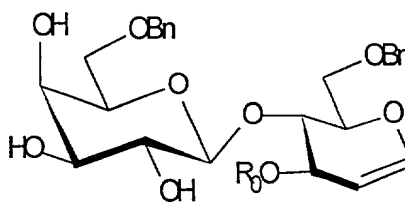
under suitable conditions to form the heptasaccharide
glycal.

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41. The method of claim 40 wherein the conditions of the reacting step
comprise an ionizing agent.

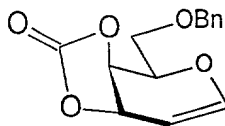
42. The method of claim 41 wherein the ionizing agent is AgBF_4 .

43. A method of preparing a protected disaccharide having the structure:



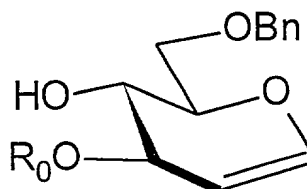
wherein R_0 is C_{1-9} linear or branched chain alkyl, arylalkyl, trialkylsilyl, arylalkylsilyl, diarylalkylsilyl, and triarylsilyl, which comprises:

(a) (i) epoxidizing a galactal carbonate having the structure:

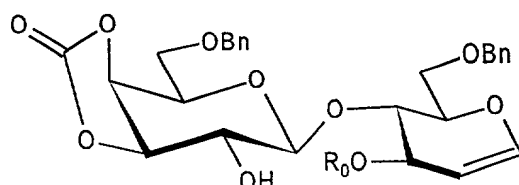


with an oxygen transfer agent under suitable conditions to form an epoxide galactal; and

(ii) coupling the epoxide galactal formed in step (a) (i) with a doubly protected galactal having the structure:



under suitable conditions to form a disaccharide carbonate having the structure:

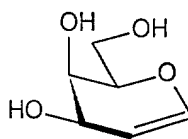


and

- (b) saponifying the disaccharide carbonate formed in step (a) (ii) under suitable conditions to form the protected disaccharide.

44. The method of claim 43 wherein the galactal carbonate is prepared by a process which comprises:

- (a) protecting a galactal having the structure:



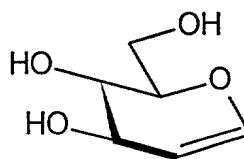
with an alkylating agent under suitable conditions to form a first protected galactal; and

- (b) treating the first protected galactal formed in step (a) with a carbonate-forming reagent under conditions suitable to form the galactal carbonate.

45. The method of claim 44 wherein the carbonate-forming reagent is $(\text{Im})_2\text{CO}$ /DMAP.

1 46. The method of claim 43 wherein the doubly protected galactal is
2 prepared by a process which comprises:

3 (a) protecting a second galactal having the structure:



8 with an alkylating agent under conditions suitable to form a
9 second protected galactal; and

10
11 (b) protecting the second protected galactal formed in step (a) with
12 an alkylating agent which may be the same or different from
13 that of step (a) under conditions suitable to form the doubly
protected galactal.

1 47. The method of claim 46 wherein each alkylating agent is independently
2 an alkyl, arylalkyl, trialkylsilyl, aryldialkylsilyl, diarylalkylsilyl or
3 triarylsilyl halide or triflate.

1 48. The method of claim 47 wherein the alkylating agent is benzyl
2 bromide.

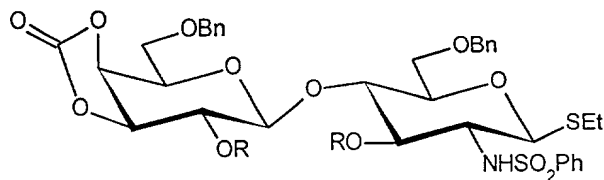
1 49. The method of claim 47 wherein the alkylating agent is TES-Cl.

1 50. The method of claim 43 wherein the oxygen transfer agent is DMDO.

1 51. The method of claim 43 wherein the conditions of the coupling step
2 comprise ZnCl_2 in THF.

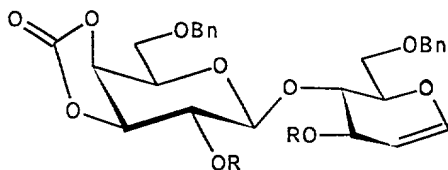
52. The method of claim 43 wherein the conditions of the saponifying step comprise K_2CO_3 in methanol.

53. A method of preparing an ethylthioglycoside having the structure:

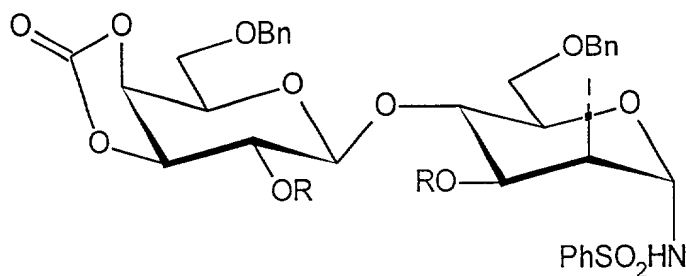


wherein R is C_{1-9} linear or branched chain alkyl, arylalkyl, trialkylsilyl, aryldialkylsilyl, diarylalkylsilyl, and triarylsilyl, which comprises:

(a) treating a protected disaccharide carbonate having the structure:



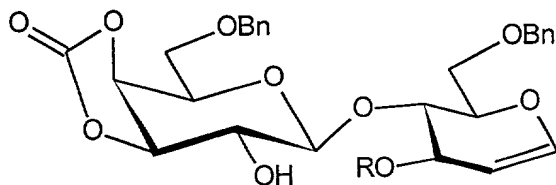
with an iodosulfonamidating agent under suitable conditions to form a disaccharide iodosulfonamidate having the structure:



and

(b) reacting the disaccharide iodosulfonamidate formed in step (a) with ethylthiol under suitable conditions to form the ethylthioglycoside.

- 1 54. The method of claim 53 wherein the protected disaccharide carbonate
 2 is prepared by a process which comprises alkylating a disaccharide
 3 carbonate having the structure:



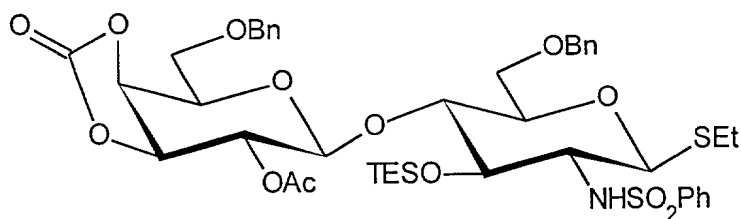
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 7
 8 with an alkylating agent under suitable conditions to form the
 9 protected disaccharide carbonate.

- 1 55. The method of claim 54 wherein the alkylating agent is an alkyl,
 2 arylalkyl, trialkylsilyl, aryldialkylsilyl, diarylalkylsilyl or triarylsilyl halide
 3 or triflate.

- 1 56. The method of claim 55 wherein the alkylating agent is TES-Cl.

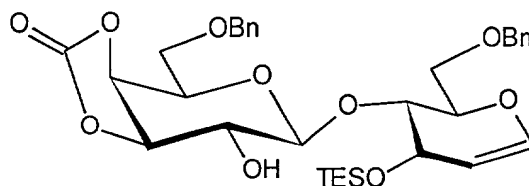
- 1 57. The method of claim 53 wherein the iodosulfonamidating agent is
 2 $I(coll)_2ClO_4$ and $PhSO_2NH_2$.

- 1 58. A method of preparing an ethylthioglycoside having the structure:

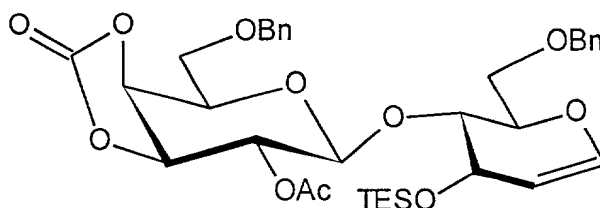


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 6
 7
 8 which comprises:

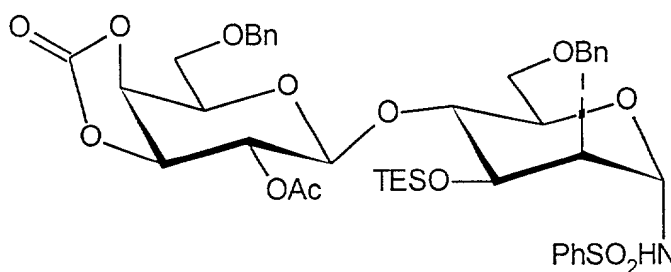
(a) acylating a disaccharide carbonate having the structure:



under suitable conditions to form an acylated disaccharide carbonate having the structure:



(b) treating the acylated disaccharide carbonate formed in step (a) with an iodosulfonamidating agent under suitable conditions to form a disaccharide iodosulfonamidate having the structure:



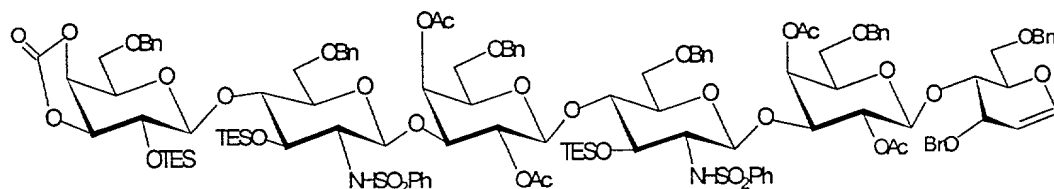
and

(c) reacting the iodosulfonamidate formed in the step (b) with ethyl thiol under suitable conditions to form the ethylthioglycoside.

59. The method of claim 58 wherein the conditions of the acylating step comprise acetic anhydride/pyridine.

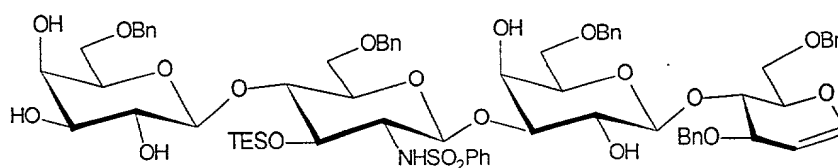
60. The method of claim 58 wherein the iodosulfonamidating agent is $I(coll)_2ClO_4$ and $PhSO_2NH_2$.

61. A method of preparing a protected hexasaccharide having the structure:

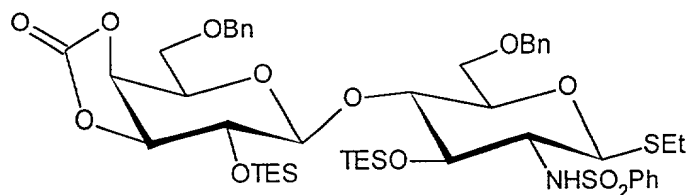


which comprises:

(a) reacting a protected tetrasaccharide having the structure:



with an ethylglycoside having the structure:

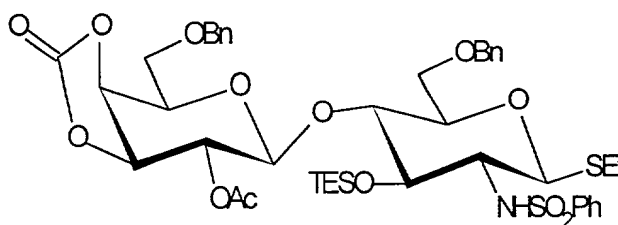


under suitable conditions to form a hexasaccharide intermediate;
and

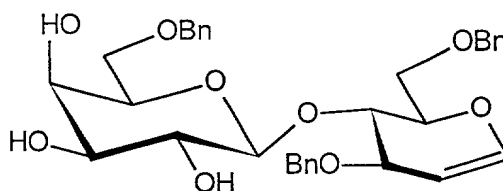
- 20 (b) acetylating the hexasaccharide intermediate formed in step (a)
 21 under suitable conditions to form the protected hexasaccharide.

1 62. The method of claim 61 wherein the protected tetrasaccharide is
 2 prepared by a process which comprises:

3 (a) coupling an ethythioglycoside having the structure:



9 with a protected disaccharide having the structure:



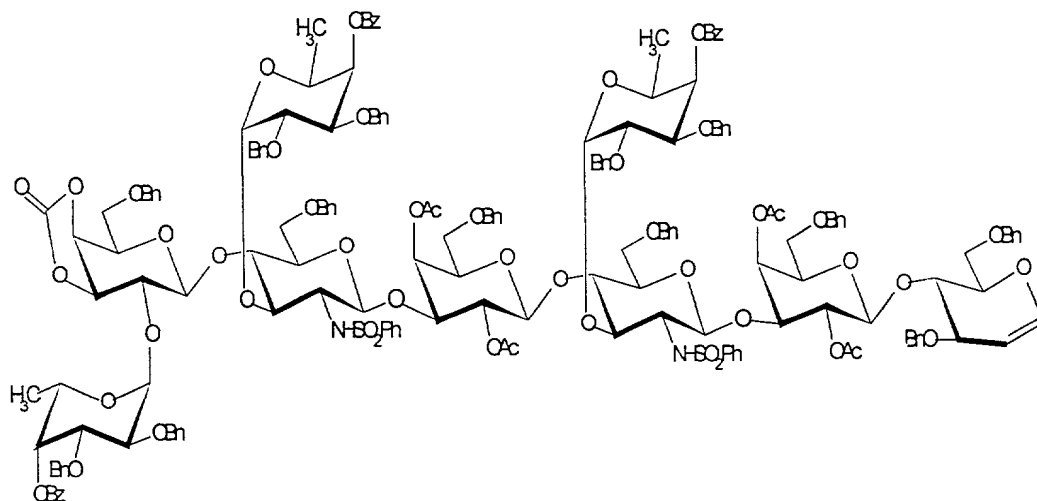
14 under suitable conditions to form a protected tetrasaccharide
 15 carbonate; and

- 17 (b) saponifying the protected tetrasaccharide carbonate formed in
 18 step (a) under suitable conditions to form the protected
 tetrasaccharide.

1 63. The method of claim 62 wherein the conditions of the coupling step
 2 comprise MeOTf/MS.

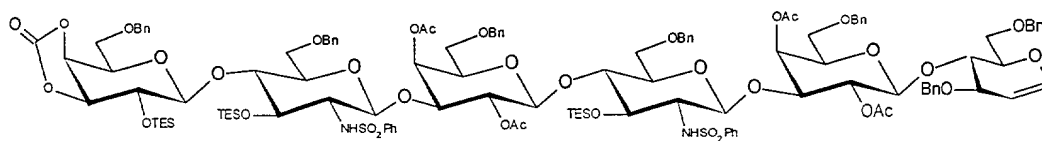
1 64. The method of claim 62 wherein the conditions of the saponifying step
 2 comprise K_2CO_3 in methanol.

65. A method of preparing a protected nonasaccharide having the structure:



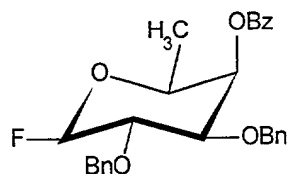
which comprises:

(a) deprotecting a protected hexasaccharide having the structure:



under suitable conditions to form a partially deprotected hexasaccharide; and

- (b) coupling the partially deprotected hexasaccharide formed in step (a) with a fucosylfluoride having the structure:



in the presence of an organometallic reagent under suitable conditions to form the protected nonasaccharide.

66. The method of claim 65 wherein the conditions of the deprotecting step comprise a fluoride salt.

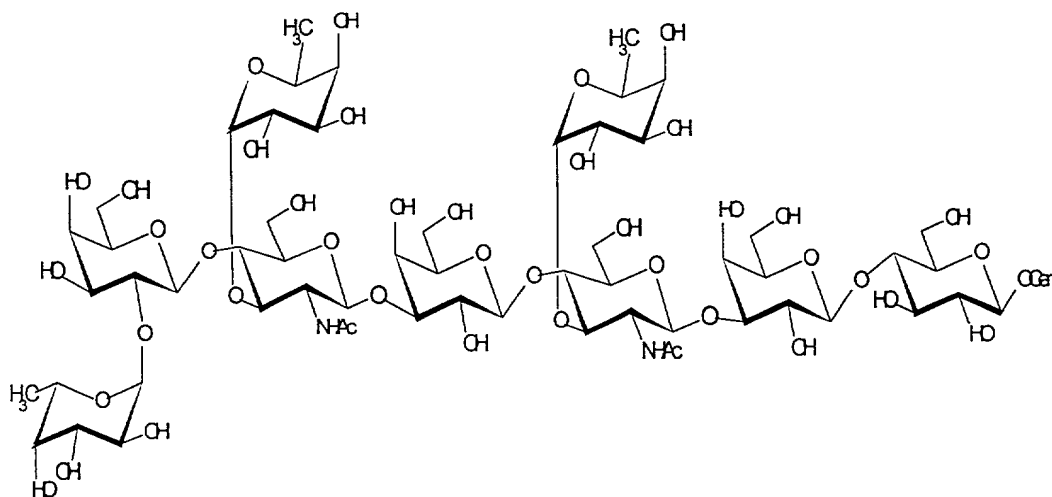
67. The method of claim 66 wherein the fluoride salt is a tetraalkylammonium fluoride.

68. The method of claim 67 wherein the fluoride salt is TBAF.

69. The method of claim 65 wherein the organometallic reagent is $\text{Sn}(\text{OTf})_2/\text{DTBP}$.

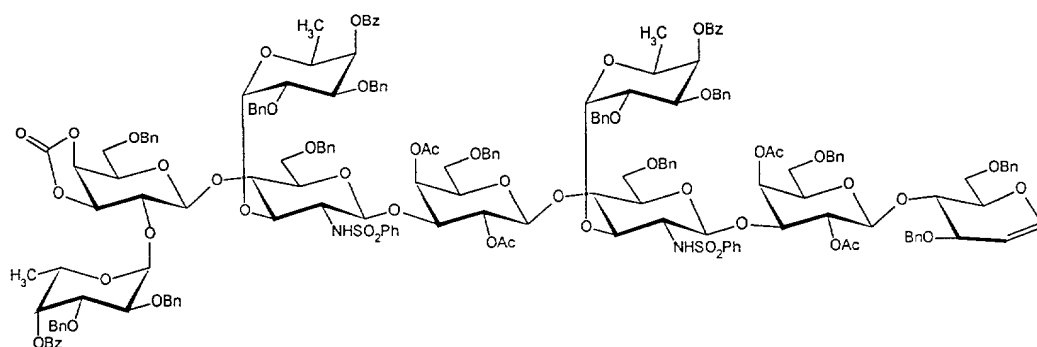
70. A method of preparing a protected nonasaccharide ceramide having the structure:

3



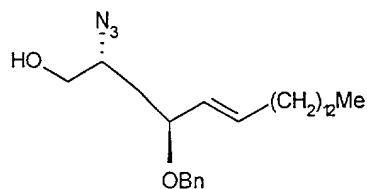
which comprises:

(a) epoxidizing a protected nonasaccharide having the structure:



with an oxygen transfer agent under suitable conditions to form a protected nonasaccharide epoxide;

(b) coupling the protected nonasaccharide epoxide formed in step (a) with an azide having the structure:



30 under suitable conditions to form a nonasaccharide azide
31 intermediate;

32

33 (c) reductively acylating the azide intermediate with palmitic
34 anhydride under suitable conditions to form a protected
35 nonasaccharide ceramide;

36

37 (d) reducing the protected nonasaccharide ceramide formed in step
38 (c) under suitable conditions to form a deprotected
39 nonasaccharide ceramide;

40

41 (e) acylating the deprotected nonasaccharide ceramide under
42 suitable conditions to form an acylated nonasaccharide
43 ceramide; and

44

45 (f) saponifying the acylated nonasaccharide ceramide under
46 suitable conditions to form the nonasaccharide ceramide.

1 71. The method of claim 70 wherein the oxygen transfer agent is DMDO.

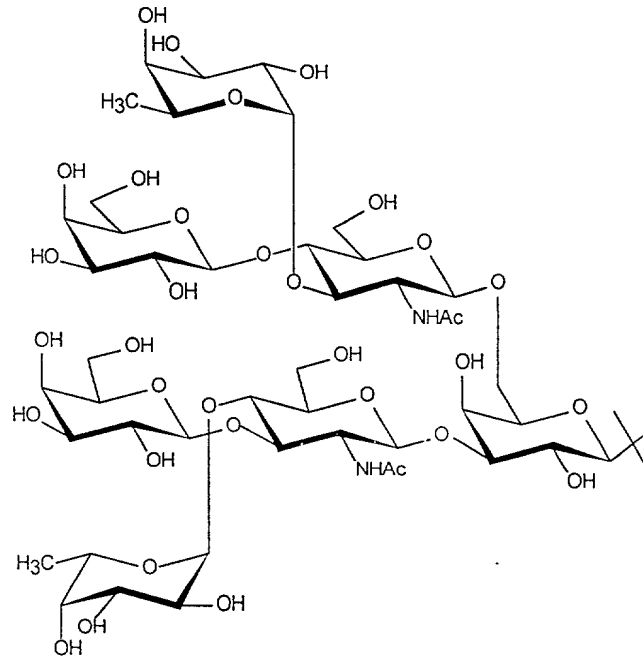
1 72. The method of claim 70 wherein the conditions of the coupling step
2 comprise ZnCl_2 .

1 73. The method of claim 70 wherein the azide intermediate is reductively
2 acylated in step (c) in the presence of Lindlar's catalyst.

1 74. The method of claim 70 wherein conditions of the saponifying step
2 comprise MeONa in methanol.

75. A method of inducing antibodies in a subject, wherein the antibodies are capable of specifically binding with epithelial tumor cells, which comprises administering to the subject an amount of a compound which contains a determinant having a structure selected from the group consisting of:

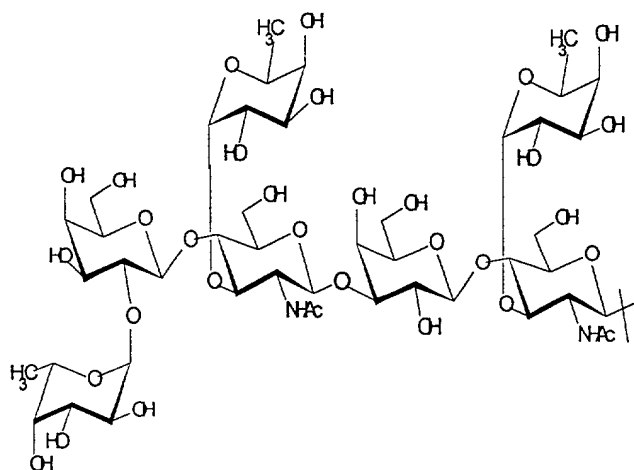
(a)



and

(b)

11



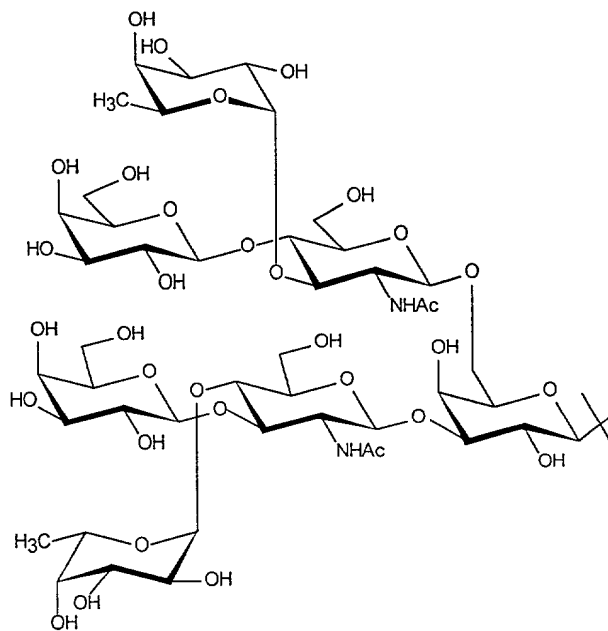
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which amount is effective to induce antibodies.

- 1 76. The method of claim 75 wherein the compound is bound to a suitable
 2 carrier protein, said compound being bound either directly or by a
 3 cross-linker selected from the group consisting of a succinimide and an
 4 M_2 linker.
- 1 77. The method of claim 75 wherein the compound contains a KH-1 or N3
 2 epitope.
- 1 78. The method of claim 76 wherein the carrier protein is bovine serum
 2 albumin, polylysine or KLH.
- 3
- 4 79. The method of claim 76 wherein the compound is a KH-1 or N3
 5 epitope.
- 1 80. The method of claim 75 which further comprises co-administering an
 2 immunological adjuvant.

- 1 81. The method of claim 80 wherein the adjuvant is bacteria or liposomes.
- 1 82. The method of claim 80 wherein the adjuvant is *Salmonella minnesota*
2 cells, bacille Calmette-Guerin or QS21.
- 1 83. The method of claim 75 wherein the epithelial tumor cells are
2 gastrointestinal tumor cells.
3
- 4 84. The method of claim 83 wherein the gastrointestinal tumor cells are
5 are colon tumor cells.
- 1 85. The method of claim 75 wherein the epithelial tumor cells are lung
2 tumor cells.
- 1 86. The method of claim 75 wherein the epithelial tumor cells are prostate
2 tumor cells.
3
- 4 87. A method of treating a subject suffering from an epithelial cell cancer,
5 which comprises administering to the subject an amount of a
6 compound which contains a determinant having a structure selected
7 from the group consisting of:

8 (a)



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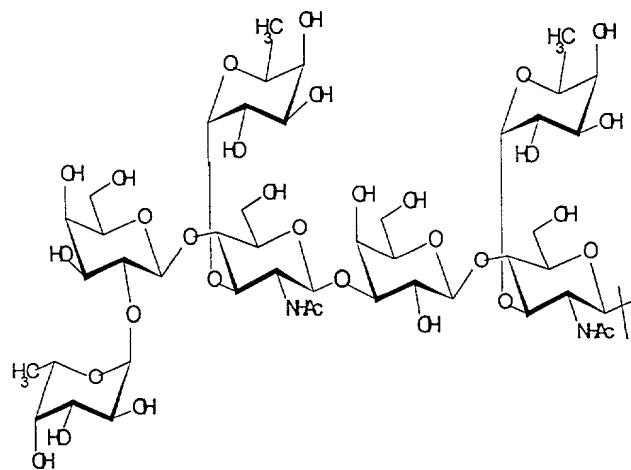
11

and

12

(b)

13



14

which amount is effective to treat the cancer.

88. The method of claim 87 wherein the compound is bound to a suitable carrier protein, said compound being bound either directly or by a cross-linker selected from the group consisting of a succinimide and an M₂ linker.

1 89. The method of claim 88 wherein the carrier protein is bovine serum
2 albumin, polylysine or KLH.

1 90. The method of claim 87 or 89 wherein the compound is contains a
2 KH-1 or N3 epitope.

1 91. The method of claim 87 or 90 which further comprises co-
2 administering an immunological adjuvant.

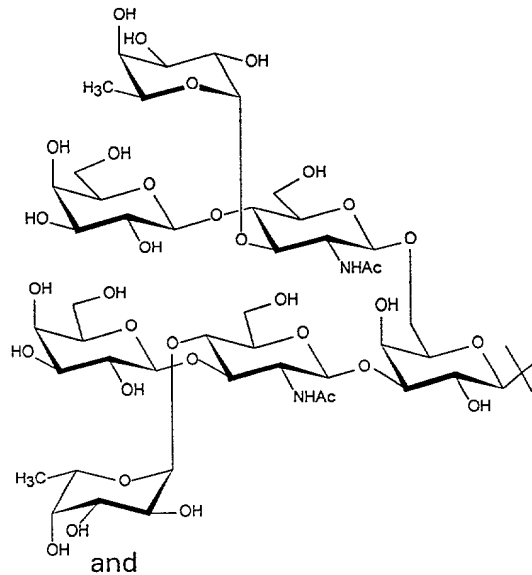
1 92. The method of claim 91 wherein the adjuvant is bacteria or liposomes.

1 93. The method of claim 91 wherein the adjuvant is *Salmonella minnesota*
2 cells, bacille Calmette-Guerin or QS21.

1 94. A method of preventing recurrence of an epithelial cell cancer in a
2 subject which comprises vaccinating the subject with a compound
3 which contains a determinant having the structure:

4 (a)

5



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7

8

(b)

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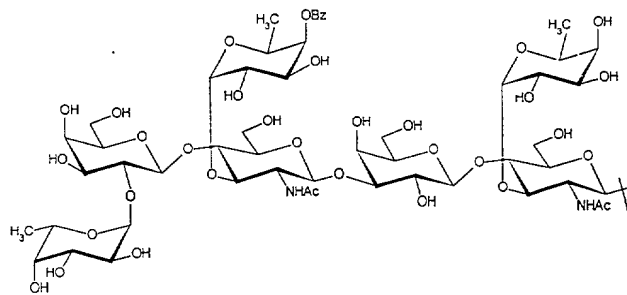
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which amount is effective to prevent recurrence of an epithelial cell cancer.

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1 95. The method of claim 94 wherein the compound is bound to a suitable
2 carrier protein.

1 96. The method of claim 94 wherein the carrier protein is bovine serum
2 albumin, polylysine or KLH.

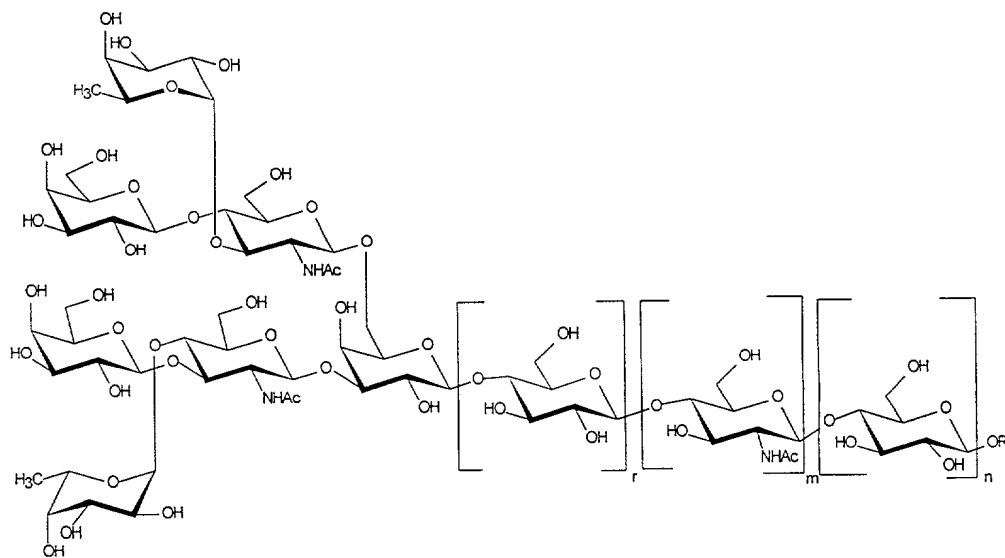
1 97. The method of claim 94 which further comprises co-administering an
2 immunological adjuvant.

1 98. The method of claim 97 wherein the adjuvant is bacteria or liposomes.

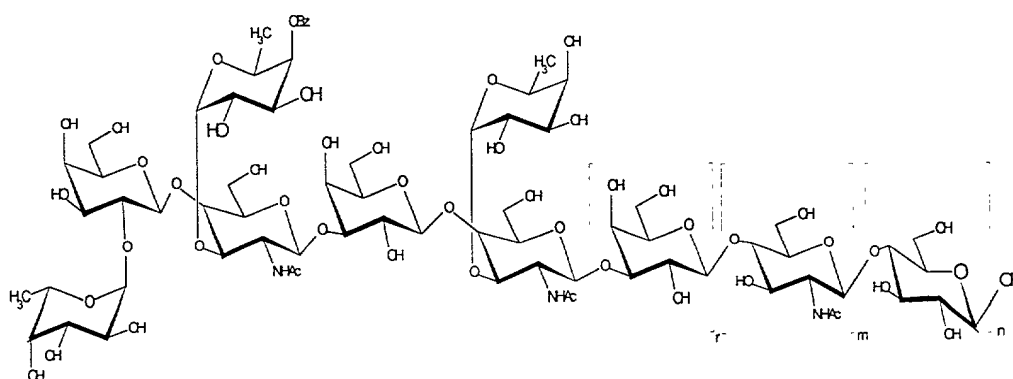
1 99. The method of claim 97 wherein the adjuvant is *Salmonella minnesota*
2 cells, bacille Calmette-Guerin or QS21.

1 100. The method of claim 75, 87 or 94 wherein the compound is selected
2 from the group consisting of:

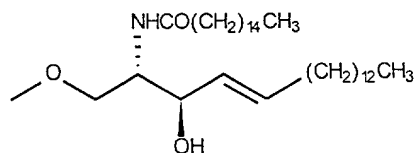
3 (a)



and



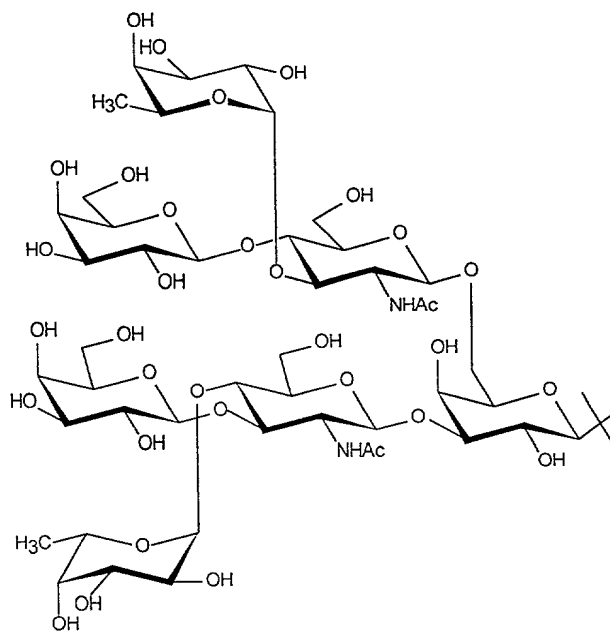
wherein R is H, substituted or unsubstituted alkyl, aryl or allyl, or an amino acyl moiety, an amino acyl residue of a peptide, an amino acyl residue of a protein, which amino acyl moiety or residue bears an ω -amino group or an ω -(C=O)- group, which group is linked to O via a polymethylene chain having the structure $-(CH_2)_s-$, where s is an integer between about 1 and about 9, or a moiety having the structure:



and wherein r, m and n are independently 0, 1, 2 or 3.

101. A composition comprising a compound which contains a determinant having a structure selected from the group consisting of:

3 (a)



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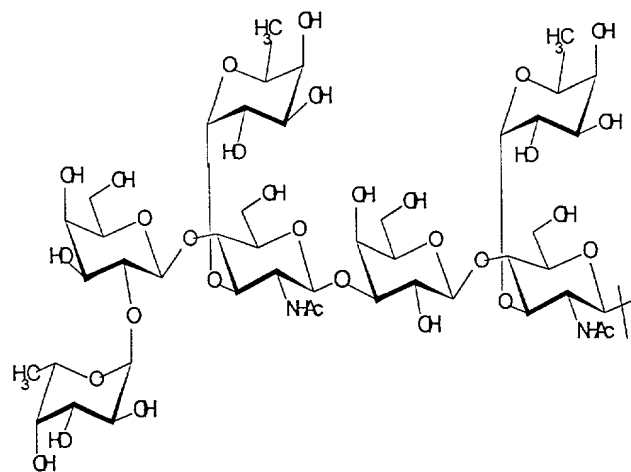
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and

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(b)

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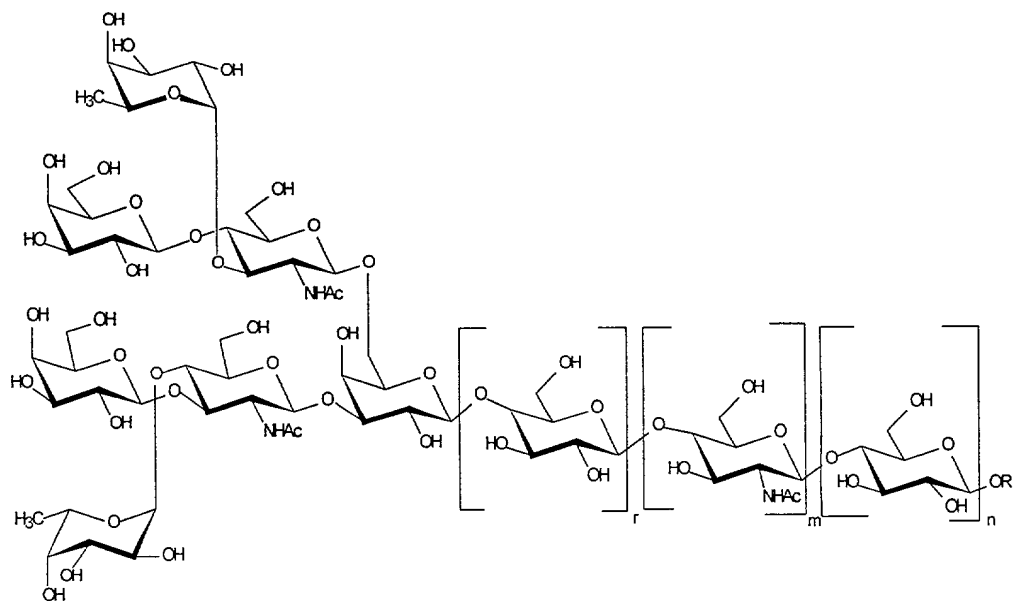
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and optionally an immunological adjuvant and/or a pharmaceutically acceptable carrier.

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- 1 102. The composition of claim 101 wherein the compound is bound to a
2 suitable carrier protein, said compound being bound either directly or
3 by a cross-linker selected from the group consisting of a succinimide
4 and an M₂ linker.
- 1 103. The composition of claim 102 wherein the carrier protein is bovine
2 serum albumin, polylysine or KLH.
- 1 104. The composition of claim 101 or 103 wherein the compound contains
2 a KH-1 or N3 epitope.
- 1 105. The composition of claim 101 wherein the immunological adjuvant is
2 bacteria or liposomes.
- 1 106. The composition of claim 105 wherein the adjuvant is *Salmonella*
2 *minnesota* cells, bacille Calmette-Guerin or QS21.
- 1 107. The composition of claim 106 wherein the compound has the
2 structure:
3 (a)

4



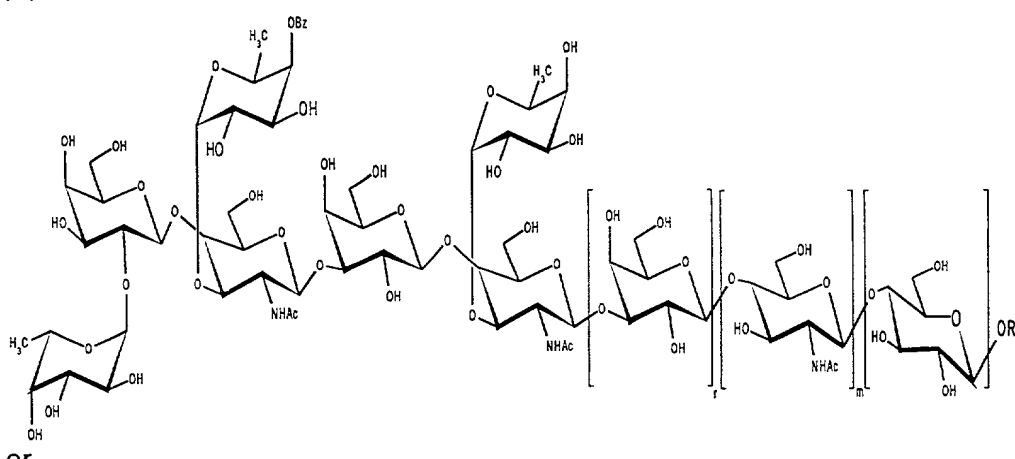
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(b)



9

10

or

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(c)

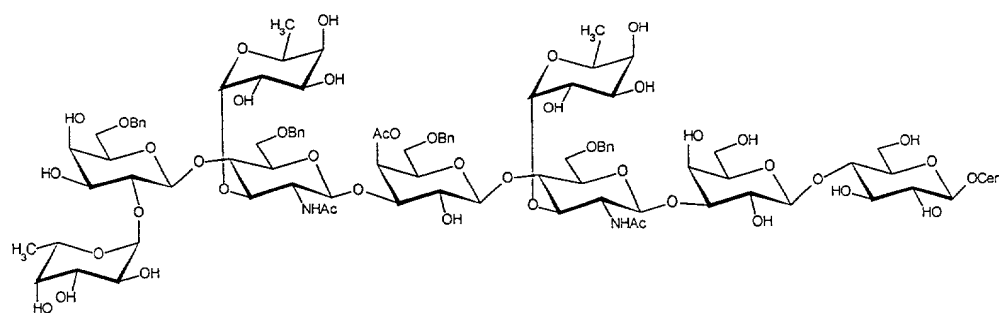
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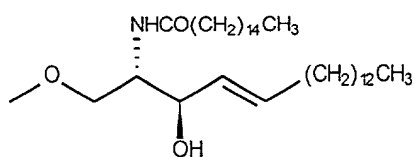
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wherein R is H, substituted or unsubstituted alkyl, aryl or allyl, or an amino acyl moiety, an amino acyl residue of a peptide, an amino acyl residue of a protein, which amino acyl moiety or residue bears an ω -amino group or an ω -(C=O)- group, which group is linked to O via a polymethylene chain having the structure $-(CH_2)_s-$, where s is an integer between about 1 and about 9, or a moiety having the structure:



and wherein r, m and n are independently 0, 1, 2 or 3.